# 2. OVERVIEW OF AEROSOL END USES AND SUBSTITUTES

## 2.1 BACKGROUND

Before 1978, CFCs were used extensively as propellants in aerosols and pressurized dispensers. Few products available today, however, are propelled with CFCs because regulatory requirements restrict the use of CFCs in aerosol applications. In 1978, EPA and the Food and Drug Administration (FDA) banned all nonessential propellant uses of CFCs in aerosol products. Some CFC aerosol products were exempted from the ban because they were determined to be essential (e.g., medical products), and some pressurized dispensers containing CFCs as the only ingredient were excluded because they did not fit the narrow definition of "aerosol propellants."

Section 610(b) of the Clean Air Act Amendments of 1990 (CAA) directs EPA to promulgate regulations that prohibit the use of Class I substances in certain "nonessential" products. In the final rule published in the *Federal Register* on January 15, 1993, EPA implemented the requirements of Section 610(b) and banned aerosol products that contain CFCs effective January 17, 1994. The rule was amended on December 30, 1993.

Under this rule, EPA exempted products from the Class I ban, including:[1]

- Medical devices listed in 21 CFR 2.125(e);
- Lubricants for pharmaceutical and tablet manufacture;
- Gauze bandage adhesives and adhesive removers;
- Topical anesthetic and vapocoolant products;
- Lubricants, coatings, or cleaning fluids for electrical or electronic equipment, which contain CFC-11, CFC-12, or CFC-113 for solvent purposes, but which contain no other CFCs;
- Lubricants, coatings, or cleaning fluids used for aircraft maintenance, which contain CFC-11 or CFC-113 as a solvent, but which contain no other CFCs;
- Mold release agents used in the production of plastic or elastomeric materials, which contain CFC-11 or CFC-113 as a solvent, but which contain no other CFCs, and/or mold release agents that contain CFC-12 as a propellant, but which contain no other CFCs;
- Spinnerette lubricant/cleaning sprays used in the production of synthetic fibers, which contain CFC-114 as a solvent, but which contain no other CFCs, and/or spinnerette lubricant/cleaning sprays which contain CFC-12 as a propellant, but which contain no other CFCs;
- Containers of CFCs used as halogen ion sources in plasma etching;
- Document preservation sprays which contain CFC-113 as a solvent, but which contain no other CFCs, and/or document preservation sprays which contain CFC-12 as a propellant, but which contain no other CFCs, and which are used solely on thick books, books with coated or dense paper and tightly bound documents; and
- Red pepper bear repellent sprays which contain CFC-113 as a solvent, but which contain no other CFCs.

It is important to note that these products exempted from the Class I ban are not exempted from phaseout requirements under the CAA.

[1] Several of the products in this list were not exempted when the final rule was published in January 1993, but were added to the list of exempted products when the Class 1 ban was amended in December 1993.

In addition to the Class I ban, Congress required EPA to promulgate regulations under Section 610(d) that prohibit the sale or distribution of aerosol products or other pressurized dispensers that contain Class II substances effective January 1, 1994.[2] Because this ban is self-implementing, EPA was not obliged to determine which products to ban. Section 610(d)(2), however, allowed EPA to grant exceptions where the use of the aerosol product or pressurized dispenser was determined to be essential as a result of flammability or worker safety, and where the only available alternative to the use of a Class II substance is the legally permitted use of a Class I substance.

In the final rule, published in the *Federal Register* on December 30, 1993, EPA exempted the products from the Class II ban, including:

- Medical devices listed in 21 CFR 2.125(e);
- Lubricants, coatings, or cleaning fluids for electrical or electronic equipment, which contains Class II substances for solvent purposes, but which contain no other Class II substances;
- Lubricants, coatings, or cleaning fluids used for aircraft maintenance, which contain Class II substances as a solvent, but which contain no other Class II substances;
- Mold release agents used in the production of plastic or elastomeric materials, which contain Class II substances as a solvent, but which contain no other Class II substances, and/or mold release agents that contain HCFC-22 as a propellant where evidence of good faith efforts to secure alternatives indicates that, other than a Class I substance, there are no suitable alternatives;
- Spinnerette lubricant/cleaning sprays used in the production of synthetic fibers, which contain Class II substances for solvent purposes and/or contain Class II substances for propellant purposes;
- Document preservation sprays which contain HCFC-141b as a solvent, but which contain no other Class II substances, and/or which contain HCFC-22 as a propellant, but which contain no other Class II substances and which are used solely on thick books, books with coated or dense paper and tightly bound documents;
- Portable fire extinguishing equipment sold to commercial users, owners of marine vessels or boats, and owners of noncommercial aircraft that contains a Class II substance as a fire extinguishant where evidence of good faith efforts to secure alternatives indicate that, other than a Class I substance, there are no suitable alternatives;
- Wasp and hornet sprays for use near high-tension power lines that contain a Class II substance for solvent purposes only, but which contain no other Class II substances; and,
- Aerosol or pressurized dispensers for cleaning fluid for electronic and photographic equipment which contain a Class II substance and is sold or distributed to a commercial purchaser.

## 2.2 USES OF OZONE-DEPLETING SUBSTANCES FOR AEROSOL APPLICATIONS

Exhibits 2-1 and 2-2 show the significance of the aerosols sector with respect to overall U.S. consumption of ozone-depleting substances (ODSs), and the relative importance of each Class I and Class II used in 1990. The consumption amounts on Exhibit 2-1 are weighted according to the chemicals' ozone depletion potentials (ODPs).[3]

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[2] All HCFCs are classified as Class II substances.

[3] Ozone depletion potential (ODP) is a relative index of the ability of a substance to cause ozone depletion. A reference level of 1.0 is assigned to CFC-11 and CFC-12. A given weight in the atmosphere of a chemical with an ODP of 0.5 would, in time, deplete half the ozone as the same weight of CFC-11 or CFC-12.

The uses of ODSs in aerosols and pressurized containers fall into two categories: propellants and solvents. The propellant category includes CFC-12, CFC-114, HCFC-22, and HCFC-142b. The solvent category includes CFC-11, CFC-113, MCF, and HCFC-141b.

The high volatility, nonflammability, and nontoxicity of CFC-12 and CFC-114 make them ideal propellants in a variety of products. Due to the 1978 ban and the restriction under the CAA, the use of CFCs as propellants has continued only in medical applications such as metered dose inhalants, contraceptive foams, and pill lubricants. Consumption of CFC-12 is estimated to have dropped to about half of its 1988 level in this sector as a result of efforts to replace it with non-CFC materials such as hydrocarbons and HCFCs. Current consumption is estimated at 2.3 million kilograms. Annual consumption of CFC-114 has declined from 1988 levels and is estimated at 0.5 million kilograms.

CFC-11 is used to dissolve active ingredients in aerosol products. Because CFC-11 evaporates quickly, it is used exclusively as a diluent and not as an active ingredient in solvent applications. CFC-11 is used in precision and general mold release agents. It is estimated that annual consumption of CFC-11 has remained roughly constant at about 1.3 million kilograms over the past few years.

CFC-113 is used as a solvent. Because it does not evaporate immediately when sprayed, it can serve as a diluent for the active ingredient or by itself as an active ingredient in aerosol products. CFC-113 can be used as a dissolving active agent in electronics solvent cleaners or as a diluent in mold release agents and lubricants. Annual consumption of CFC-113 is estimated at 3.3 million kilograms, and is believed to have remained constant over the past few years.

MCF functions similarly to CFC-113 in aerosols and pressurized containers; however, its use is more widespread. In some cases, MCF cannot replace CFC-113 because it can decompose in the presence of water to form hydrogen chloride, a corrosive acid. MCF is used as a diluent in applications such as water and oil repellents, lubricants, spray undercoats, tire shiners, insecticides, and mold release agents, or as a solvent in products such as electric motor cleaners, spot removers, brake cleaners, and electronic solvent cleaners. Current annual consumption of MCF is estimated at about 33.2 million kilograms.

As noted above, three HCFC substances are currently in use in aerosol products: HCFC-22, HCFC-142b, and HCFC-141b. HCFC-22, acting as a propellant, is the most widely used HCFC in aerosol products. The aerosol industry has adopted HCFC-22 and mixtures with HCFC-142b and dimethyl ether (DME) as replacements for CFC-12 propellants in some products. The aerosol industry's transition from CFC-12 to HCFC-22 was largely accomplished during 1990 and1991. Consumption of HCFC-22 in aerosol products in the U.S. is estimated at 5.1 million kilograms per year. This represents about 90 percent of the total estimated HCFC usage in aerosol products.[4]
exhibit 2-1

[4] It is estimated that the current annual U.S. consumption of HCFC-142b and HCFC-141b is about 0.5 and 0.05 million kilograms, respectively.

exhibit 2-2

## 2.3. SUMMARY OF ALTERNATIVES

This background document examines substitutes for CFC-11, CFC-113, MCF, and HCFC-22. Substitutes for CFC-12 and CFC-114, used as propellants in medical applications, are not discussed because substitutes for these applications are currently being developed and it is not clear which substitutes will ultimately be used. Substitutes for CFC-12 and CFC-114 in these applications will also have to undergo FDA approval, which is expected to take from three to five years. This report does not discuss substitutes for HCFC-141b and HCFC-142b because of their relatively limited use.

A variety of chemicals are currently being considered or are being used as substitutes for Class I and II controlled substances used in aerosols and pressurized containers. The suitability of alternatives depends upon the product in which they are used. Each of these alternatives has its own properties such as solvency, flashpoint, performance, costs, and environmental considerations that allow it to replace Class I and II substances in certain aerosol products. The majority of substitutes considered to replace ODSs are currently available and easily integrated into existing aerosol production facilities.

### 2.3.1 Propellant Substitutes

The primary substitutes for the propellant uses of HCFC-22 and HCFC-142b are:

- Hydrocarbons;
- HFCs;
- HFC/Dimethyl ether blends;
- Compressed gases; and
- Not-in-kind systems.

**Hydrocarbons** are promising replacements for nonessential uses of HCFC-22 as a propellant in aerosols and pressurized containers. Because these small chain compounds such as butane, isobutane, and propane have low boiling points, they perform well as propellants. Hydrocarbon propellants are used separately or in mixtures, are inexpensive (four times less expensive than HCFC-22), and are readily available from most chemical distributors.

The major area of concern with hydrocarbons is their flammability. In applications where a nonflammable propellant is needed, a hydrocarbon could not be used. For example, the use of hydrocarbons around electrical equipment could prove hazardous if sparks from the equipment were to ignite the hydrocarbon propellant.

Hydrocarbons are adequate substitute propellants where flammability is not a concern. To reduce product flammability, hydrocarbons can be used with water-based formulations in products such as insecticides accompanied by slight reductions in product quality. Manufacturers are also hindered from selling hydrocarbon-propelled aerosols in certain jurisdictions. In California, for example, the use of hydrocarbons is restricted because of their classification as volatile organic compounds which contribute to low level ozone or smog.

**HFCs** such as HFC-125, HFC-134a, and HFC-152a are recently-developed, partially fluorinated hydrocarbons. These compounds are less dense than HCFC-22 but can function well as propellants with minor reformulation adjustments. Because HFCs have only recently been developed, they are not readily available and are expected to be priced significantly higher than HCFC-22 -- around ten times more expensive. With increased economies of scale, HFCs should become less costly and more attractive as substitutes.

**HFC/DME** blends such as HFC-152a/DME are being tested for use in safety sprays and animal repellants. Both HFC-152a and DME are flammable, but the flammability of the HFC-152a/DME formulation is not well understood at this time.

**Compressed gases** such as carbon dioxide, nitrogen, air, and nitrous oxide are low molecular weight gases that can be used as propellants in aerosol products; however, they cannot serve as drop-in replacements for HCFC-22. First, alternative dispensing mechanisms and stronger containers are needed because these gases are under significantly higher pressure. Containers holding compressed gases are, by necessity, larger and bulkier. Second, because these chemicals have low molecular weights, they are inadequate as replacements for HCFC-22 in products requiring a dense gas propellant, such as noise horns, or in products requiring fine dispersion of the product, such as surface lubricants and weld inspection developers. Third, compressed gases, under high pressure, dispel material faster, which contributes to wasted product.

Compressed gases are inexpensive and readily available from most chemical distributors. Upon expansion, compressed gases are quite cool. This property could be exploited in products such as freezants and gum removers, so that compressed gases could substitute for some nonessential uses of HCFC-22. Also, compressed gases are nonflammable and can serve as propellants in applications where a nonflammable propellant is necessary, although not in applications where a fine, evenly-dispersed spray is required.

**Not-in-kind** systems such as manually operated pumps and sprays provide an alternative delivery mechanism to the aerosol dispenser. Development of not-in-kind replacements depends on technological feasibility. Some products, such as aerosol foams, cannot be easily formed with not-in-kind systems. In other products, the not-in-kind system may not provide proper dispersion or accurate application of the product, limiting its use. The success of not-in-kind systems depends, in large part, on consumer or worker preferences. Persons using manual pumps or sprays (in applications where not-in-kind systems function adequately as replacements) may tire or become fatigued with the pumping motion. Such drawbacks reduce consumer satisfaction and subsequent use. Not-in-kind systems would not easily replace the use of aerosols in applications where it is not technologically feasible or where the product is used repeatedly.

### 2.3.2 Solvent Substitutes

The primary substitutes for the solvent/diluent uses of CFC-11, CFC-113, MCF, and HCFC-141b are:

- HCFC-141b;
  - Petroleum-based hydrocarbons;
  - Oxygenated hydrocarbons;
  - Chlorinated solvents;
  - Terpenes; and
  - Water-based systems.

**HCFC-141b** is a potential substitute for CFC-11 and CFC-113 used in solvent/diluent applications in aerosols and pressurized dispensers. It is unlikely that manufacturers would use HCFC-141b as a substitute for MCF because the two compounds have similar ODPs.

HCFC-141b has a number of characteristics that make it a suitable alternative solvent: it is nonconductive, nonflammable, and highly evaporative. HCFC-141b is expensive compared to the pre-tax price of CFC-113 (almost three times the cost). In addition, HCFC-141b is slightly corrosive to plastics parts, and cannot serve as a drop-in replacement for all the solvent uses of CFC-11 and CFC-113.

**Petroleum-based hydrocarbons** are hydrocarbons fractionated from the distillation of petroleum. These compounds are loosely grouped into paraffins (six carbon chains to ten carbon chains — hexane, n-heptane, etc.) and light aromatics (toluene and xylene) and come in various levels of purity. These compounds are good solvents that are relatively inexpensive (costing about half as much as MCF)[5] and are readily available from chemical distributors. Petroleum-based hydrocarbons can substitute for controlled substances that function solely as diluents (such a those used in automotive undercoating applications) with only minor reformulation changes. Many of the products containing petroleum-based hydrocarbons even outperform their chlorinated counterparts. Petroleum-based hydrocarbons are flammable, however, and cannot be used as replacement solvents in applications where the solvent must be nonflammable, such as electronics cleaning applications.

**Oxygenated hydrocarbons** are molecules based on hydrocarbons containing appendant oxygen (alcohols and ketones), integral oxygens (ethers), or both (esters). These compounds are relatively inexpensive (about half the cost of MCF) and are readily available from chemical distributors. They are also flammable, making them unsuitable for some applications.

These compounds are currently being blended with Class I substances to reduce the amount of Class I substances used in a product formulation. Since the quantity of these compounds is small, the product still remains nonflammable. Some manufacturers are, however, completely reformulating products such as spot removers with oxygenated hydrocarbons. To continue the use of these convenient products, consumers may have to be educated about the product's increased flammability.

**Chlorinated solvents** such as perchloroethylene, trichloroethylene, and methylene chloride can be used to replace CFC-11, CFC-113, and MCF in solvent applications in aerosol and pressurized containers. Because chlorinated solvents are strong solvents, they are able to dissolve compounds that are difficult to dissolve in other solvents such as fluorinated polymers. Due to toxicity concerns, these compounds will probably not be used in products sold to the general public.

Because chlorinated solvents are nonflammable and are strong solvents, they are promising substitutes for ODSs in electronic equipment or electric motor cleaning applications where safeguards could protect workers from fumes. These compounds are priced comparably to MCF and are readily available from chemical distributors.

**Terpenes** are unsaturated hydrocarbons based on isoprene subunits with good solvent properties. While flammability concerns must be addressed, these compounds can replace ODSs in some applications. Some terpenes have a slight citrus scent while others have stronger odors, making them unpleasant to work with.

**Water-based systems** can replace the use of CFC-11, CFC-113, and MCF as solvents in aerosols and pressurized dispensers. These reformulated products usually contain new components/active ingredients that are water soluble. The overall function of the reformulated product remains the same, but the product's constituents are changed.

Most water-based products are nonflammable and can be used to replace ODSs as solvents in aerosol applications around sources of ignition such as an open flame. They cannot be used around sources of electricity, however, because they tend to be conductive and could short-out electrical equipment. Water-based products may also have short shelf-lives as the active ingredient may decompose in an aqueous environment. Also, these products do not evaporate quickly. Consequently, product accumulates on surfaces on which it is sprayed. This may present a problem in certain

[5] Pre-tax prices for CFC-11, CFC-113, and MCF were about \$.90, \$2.90, and \$.40 per pound respectively in 1991 (EPA 1992).

applications where the accumulation of a water-based product contributes to rust or corrosion. The possibility of reformulating products is product-specific, depending on the feasibility of finding active ingredients that are water soluble.

## CHAPTER 2 REFERENCES

U.S. EPA. 1992. *Draft Background Document on Aerosol and Foam Products That Contain Class II Substance*. Office of Air and Radiation, Global Change Division. March, 1992.